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13. ABSTRACT (Maximum 200 words) <p>A series of monometallic and bimetallic transition metal complexes have been synthesized for incorporation into highly conductive and potentially superconductive materials. Studies of $\text{Ni}(\text{dmit})_2(\text{C}^+)_x$, as a function of cation (C^+) type, have allowed elucidation of the effect of structure on electronic properties. A new class of bimetallic tetrathiooxalate (tto) bridged compounds were discovered that form new synthetic conductors. For example, the reaction of $\text{Bu}_4\text{N})_2\{\text{tto}[\text{Ni}(\text{dmit})]_2\}$ with $(\text{TTF})_3(\text{BF}_4)_2$ led to a material with a conductivity of 0.4 S/cm. A full study of seven new bimetallic, and one new tetrametallic, complex has been carried out with single crystal X-ray structures determined.</p>				
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AFOSR FINAL PROGRESS REPORT

**MONOMETALLIC AND BIMETALLIC CHALCOGEN-RICH,
EXTENSIVELY CONJUGATED AND PLANAR COMPLEXES FOR
HIGHLY ELECTRICALLY CONDUCTING MATERIALS**

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Objectives

We are carrying out the synthesis of new transition metal complex anion-radical salts for superconducting complexes, while studying the electrocrystallization, structure and electronic properties of their charge-transfer salts. We have synthesized a series of Cu(II) and Ni(II) bimetallic, extensively conjugated and chalcogen-rich complexes as new precursors to electrically conducting and even superconducting materials.

Status of Effort

In the course of the project, significant progress has been made in the synthesis, characterization, and properties studies of highly electrically conducting, anion-radical salt complexes. The complexes are composed of extensively conjugated and planar, chalcogen-rich ligands, and square planar coordinating metals.

The first phase of research has focused on Ni(dmit)₂ based bis-chelate complexes. The complexes (Bu₄N)₂[Ni(dmit)₂]₇·2CH₃CN (1), (Me₃S)[Ni(dmit)₂]₂ (2), (Ph₄P)[Ni(dmit)₂]₃ (3) and (MePh₃P)[Ni(dmit)₂]₃ (4), have been electrocrystallized and characterized by X-ray diffraction. The electronic and optical properties have been studied utilizing conductivity versus temperature and reflectance spectroscopy. All four materials are semiconductors.

The second phase of the work has been the design and synthesis of new extensively and conjugated, chalcogen-rich, bimetallic copper(II) and nickel(II) complexes. The complexes with the general formula (Bu₄N)₂{tto[M(L)]₂} (where M = Cu(II), L = dmit (5), mnt (6), dsit (7), dmtd (8); M = Ni(II), L = dmit (9), dsit (10), dmise (11)), have been characterized X-ray diffraction and cyclic voltammetry. Conductivities of the partially oxidized complexes have been studied and show the insulating as made dianionic species to increase in conductivity over eight orders of magnitude.

Using the same synthetic methodology, attempts were made to synthesize a new bimetallic copper(II) complex with dmt as the capping ligand. The interesting tetrameric

copper complex, $(\text{Bu}_4\text{N})_2[\text{Cu}(\text{dmt})]_4$ (12), was synthesized and characterized by X-ray diffraction and cyclic voltammetry.

Accomplishments/New Findings

A. Optical and transport properties of 1, 2, 3, and 4. During the course of the project, a comprehensive study of the transport and optical properties of the constant current electrocrystallized complexes 1 - 4 was completed. Spectroscopic methods are well suited to the study of these highly anisotropy materials. The methods provide information on both the electronic charge transfer and localized excitations at high energies as well as the vibrational features at low energies.

Figure 1 shows the packing arrangement of 3 and Figure 2 of 4, two of the complexes studied. The dc conductivity versus temperature results display semiconducting behavior for all four $\text{Ni}(\text{dmit})_2$ based complexes (Figure 3).

The frequency dependent conductivity was also studied from reflectance spectroscopy data via Kramers-Kronig analysis of complexes 1, 2, and 3 as seen in Figure 4. Complex 4 could not be studied by this method due to the inability to obtain crystals of suitable quality. The general behavior of the spectra displays a broad low-energy band which contains a majority of the oscillator strength and several weak electronic features at higher frequencies for the complexes along the $\text{Ni}(\text{dmit})_2$ stacking direction. Another feature is the fact that in all cases, they show a conductivity maximum at finite frequency in contrast to the simple Drude behavior of the ordinary metals. The conductivity maximum shifts to higher frequencies as the mid-infrared reflectance level decreases and as the dc conductivity also decreases.

B. $(\text{Bu}_4\text{N})_2\{\text{tto}[\text{Cu}(\text{dmit})]_2\}$ (5), $(\text{Bu}_4\text{N})_2\{\text{tto}[\text{Cu}(\text{mnt})]_2\}$ (6), $(\text{Bu}_4\text{N})_2\{\text{tto}[\text{Cu}(\text{dsit})]_2\}$ (7), and $(\text{Bu}_4\text{N})_2\{\text{tto}[\text{Cu}(\text{dmid})]_2\}$ (8). The complexes tetrabutylammonium(μ -tetrathiooxalato) bis[(2-thioxo-1,3-dithiole-4,5-

dithiolato)cuprate(II)] (5), tetrabutylammonium(μ -tetrathiooxalato) bis[(1,2-dicyanoethene-1,2-dithiolato)cuprate(II)] (6), tetrabutylammonium(μ -tetrathiooxalato) bis[(2-thioxo-1,3-dithiole-4,5-diselenolato)cuprate(II)] (7), and tetrabutylammonium(μ -tetrathiooxalato) bis[(2-oxo-1,3-dithiole-4,5-dithiolato)cuprate(II)] (8) shown in Figure 5, were assembled using a unique and facile, three-solvent synthesis. Intrachain S...S interactions are observed as a result of head-to-tail contacts between thiole-thioxo, selenone-thioxo, and thiole-oxo groups of adjacent dianionic units in complexes 5, 7, and 8 (Figure 6). Complex 6 is the first fully planar tetrathiooxalato-bridged complex synthesized (Figure 7). Complexes 5, 7 and 8 are not completely planar with dihedral angles formed between the planes of the tto bridging ligands and capping ligands due to a tetrahedral distortion at the metal centers.

The redox behavior of 5 - 8 was examined by cyclic voltammetry (CV) in 0.1 M TBAP/CH₂Cl₂ at a Pt working electrode. The CV data shows two reversible low potential waves for all of the complexes. $E_{1/2}$ values for the first redox process range from -0.79 to -0.63 V (vs Ag/AgCl) and -0.15 to 0.00 V for the second redox process. Further oxidation processes are observed at higher potentials which may be attributed to the formation of a cationic species. Electrocrystallization experiments carried out show the deposition of insoluble powder on the electrode surface.

To determine the conductivity of partially oxidized complexes, the reactions of 5 with varied amounts of NaI/I₂ in acetone followed by precipitation with methanol were carried out. To date, these reactions have yielded black powders with pressed pellet conductivities up to 10⁻² S/cm. This is at least eight orders of magnitude higher than the single-crystal conductivities of <10⁻¹⁰ S/cm. Elemental analysis data shows the formation of a complex with stoichiometry (Bu₄N)_{0.33}{tto[Cu(dmit)]₂}.

C. (Bu₄N)₂{tto[Ni(dmit)]₂} (9), (Bu₄N)₂{tto[Ni(dsit)]₂} (10), and (Bu₄N)₂{tto[Ni(dmise)]₂} (11). The complexes tetrabutylammonium(μ -

tetrathiooxalato) bis[(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(II)] (9), tetrabutylammonium(μ -tetrathiooxalato) bis[(2-thioxo-1,3-dithiole-4,5-diselenolato)nickelate(II)] (10), and tetrabutylammonium(μ -tetrathiooxalato) bis[(2-selenoxo-1,3-dithiole-4,5-dithiolato)nickelate(II)] (11) shown in Figure 8 were assembled using a different synthetic methodology than for 5 - 8. The reaction of $(\text{Et}_4\text{N})_2\text{tto}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and the dicesium salt of the ligand of choice in acetone yielded complexes 9 - 11. The dianionic units of the complexes form two-dimensional nonbonding arrays. The packing diagram of $(\text{Bu}_4\text{N})_2\{\text{tto}[\text{Ni}(\text{dsit})]_2\}$ (10) is shown in Figure 9.

The redox behavior of 9 - 11 was examined by cyclic voltammetry (CV) in 0.05 M $\text{Me}_4\text{NClO}_4/\text{CH}_3\text{CN}$ at a Pt working electrode. All of the complexes exhibit a first low potential reversible redox wave followed by a second non-reversible redox process indicative of deposition-redissolution behavior. $E_{1/2}$ values for the first redox process are approximately the same for all of the complexes (~ -0.82 V vs Ag/Ag^+) while the second oxidation peak for 9 - 11 occurs in the range of -0.23 to -0.15 V.

The compound $(\text{Bu}_4\text{N})_2\{\text{tto}[\text{Ni}(\text{dmit})]_2\}$ (9) was reacted with $(\text{TTF})_3(\text{BF}_4)_2$ in CH_3CN and yielded a black insoluble precipitate. Pressed-pellet conductivity measurements were completed and the material was found to have a value of 0.4 S/cm. Electrocrystallization experiments have been carried out with 9 and have yielded black microcrystalline material on the anode. The elemental composition and conductivity properties of these materials are currently being investigated.

D. $(\text{Bu}_4\text{N})_2[\text{Cu}(\text{dmt})]_4$ (12). The three-solvent reaction $(\text{Bu}_4\text{N})[\text{Zn}(\text{dmt})_2]$ (CH_2Cl_2) with $(\text{Et}_4\text{N})_2\text{tto}$ (H_2O) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (MeOH) yielded the tetrameric, dianionic complex (Figure 10). The coordination geometry of each of the copper ion metal centers is distorted tetrahedral. The dmt ligand coordinated in a unique fashion not observed in other dmt ligand complexes. Four copper atoms and four sulfur atoms

compose a planar, eight-membered ring core. The dianions pack in a columnar array with S...S nonbonding interactions on adjacent molecules.

The redox behavior of **12** was investigated by cyclic voltammetry (CV) in 0.1 M TBAP/CH₂Cl₂ at a Pt working electrode. The CV data exhibits two anodic processes ($E_{p,a}$ = 0.15 and 1.05 V vs Ag/Ag⁺) correlated with two cathodic processes ($E_{p,c}$ = -0.45 and -0.75 V). This suggests that higher oxidation states may be obtained.

FIGURE 1

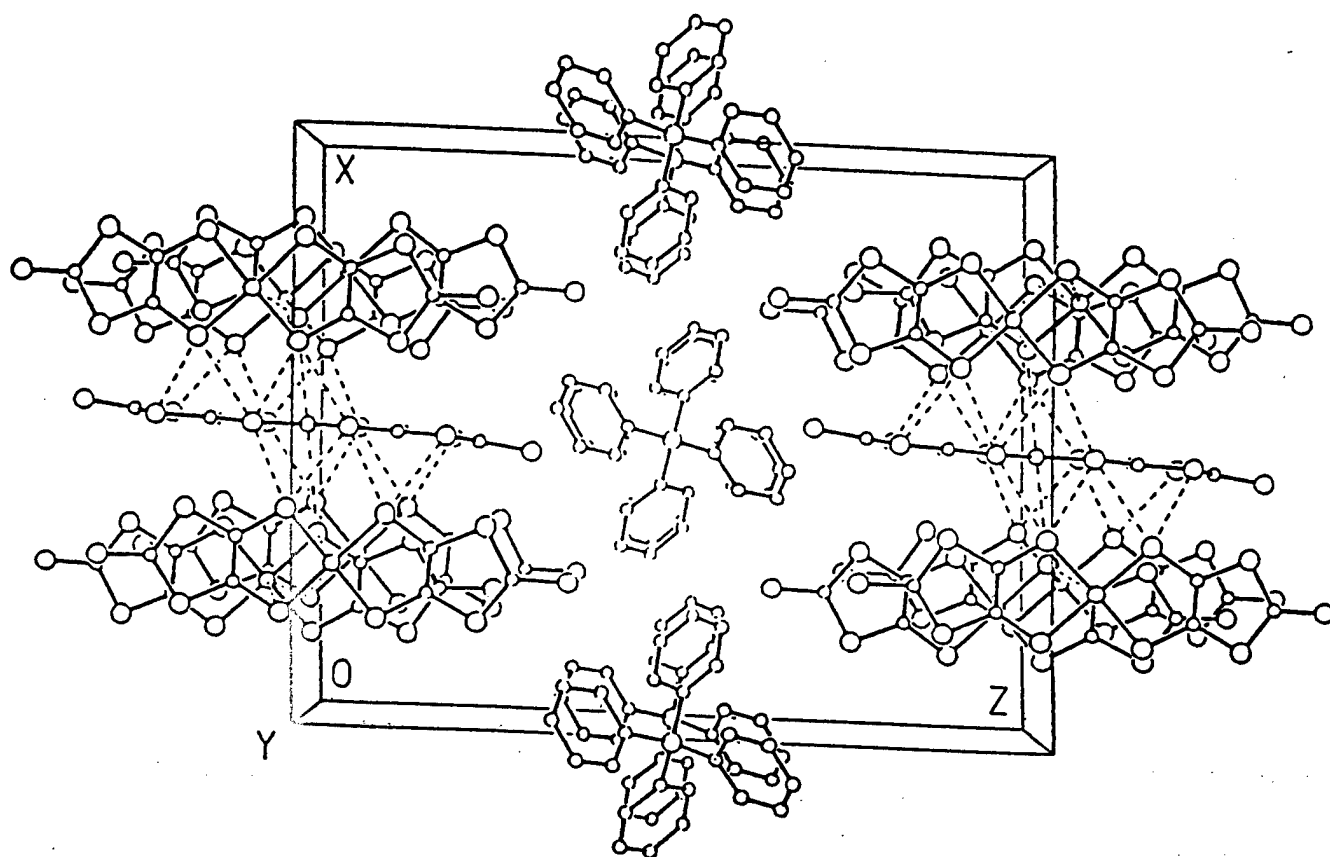


FIGURE 2

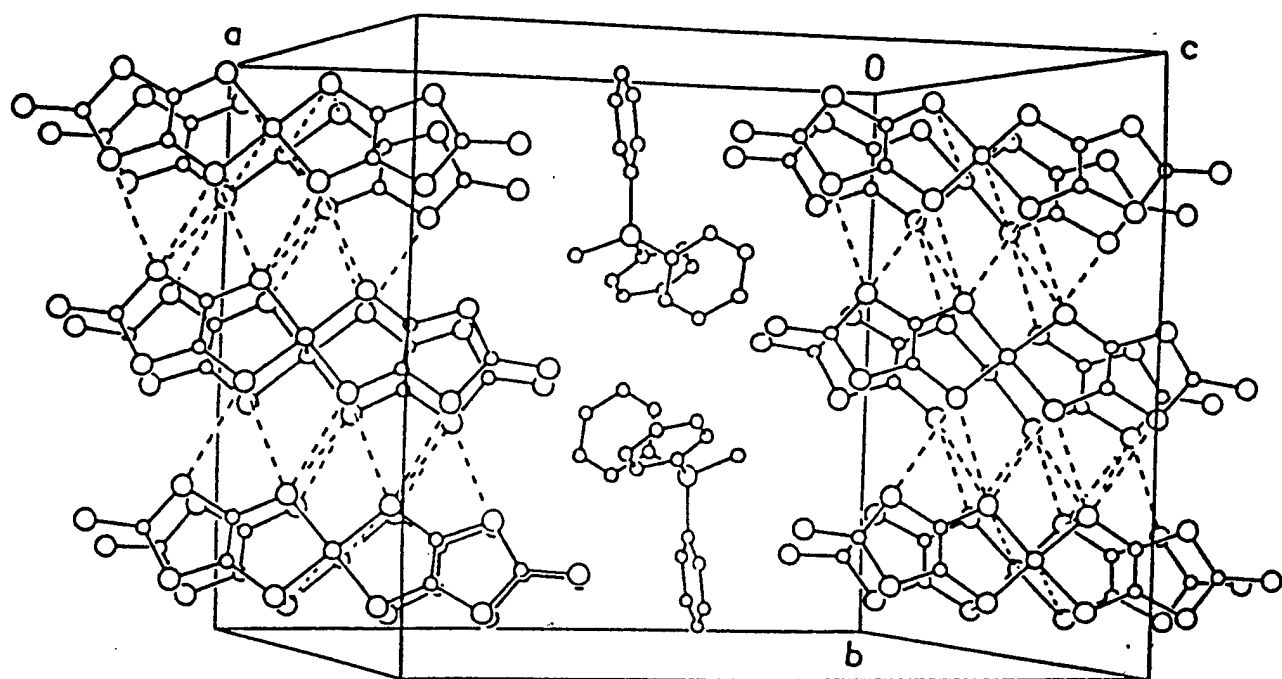


FIGURE 3

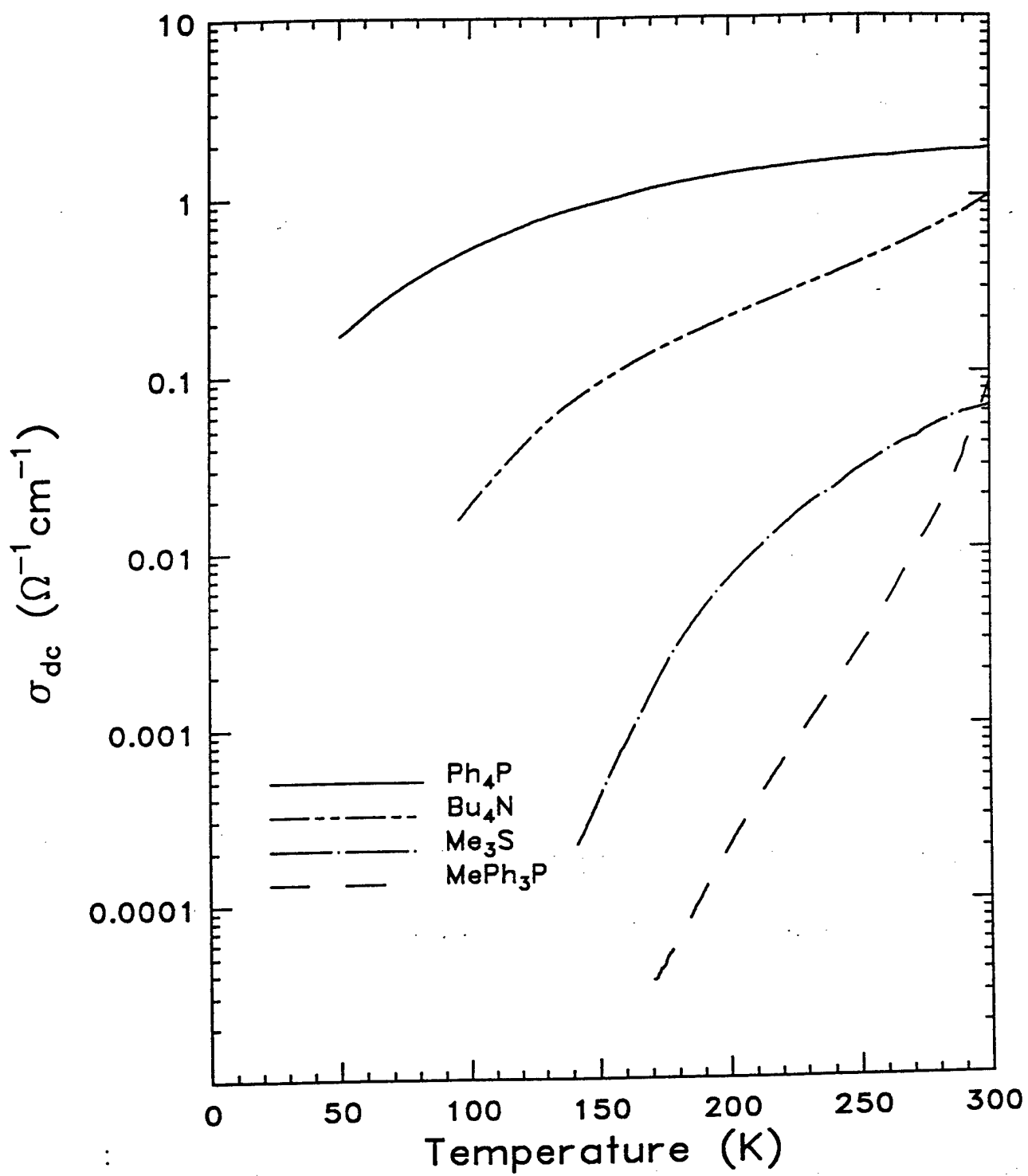


FIGURE 4

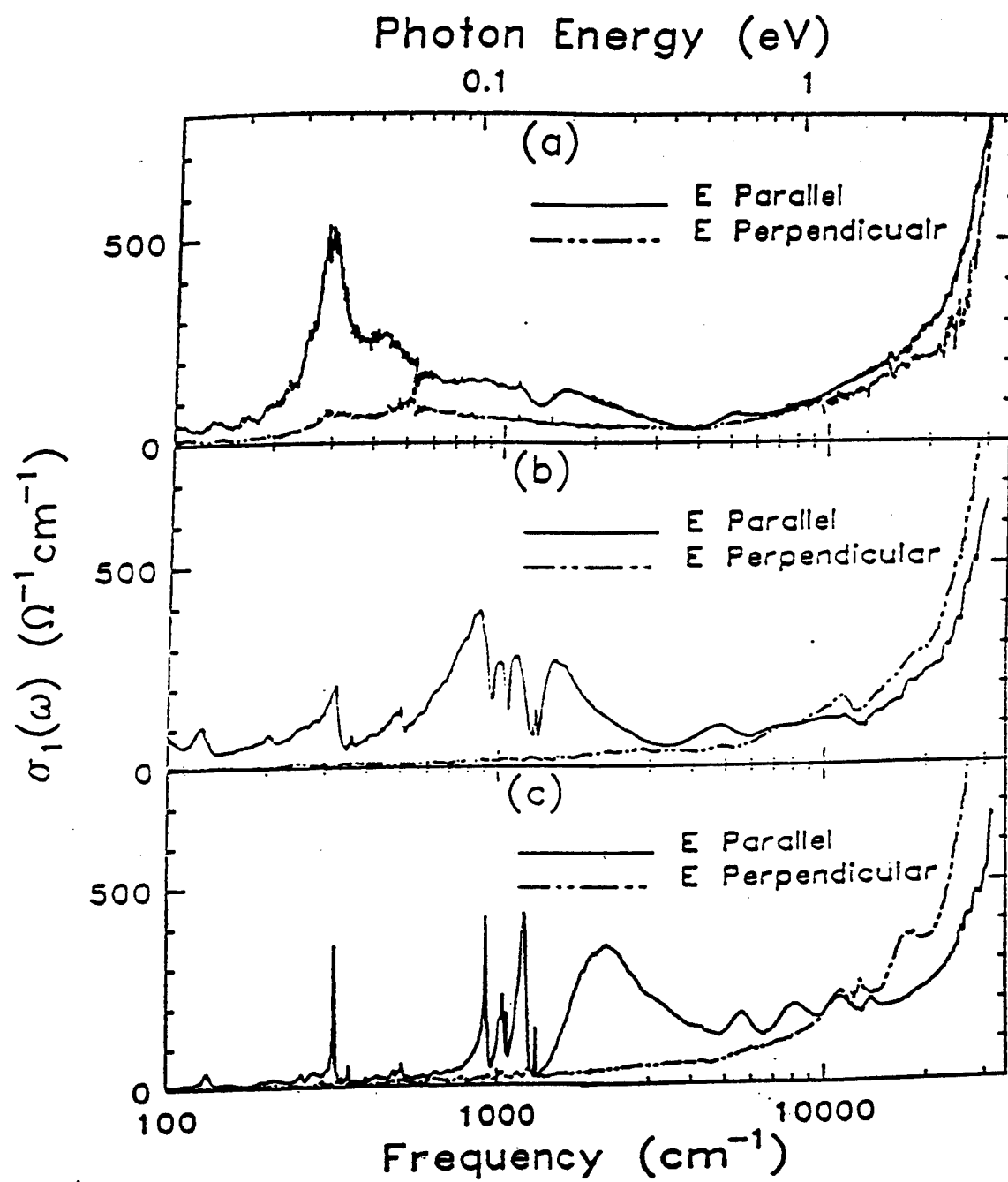
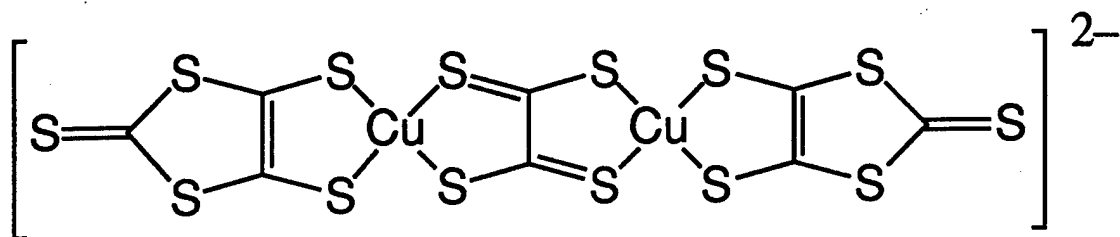
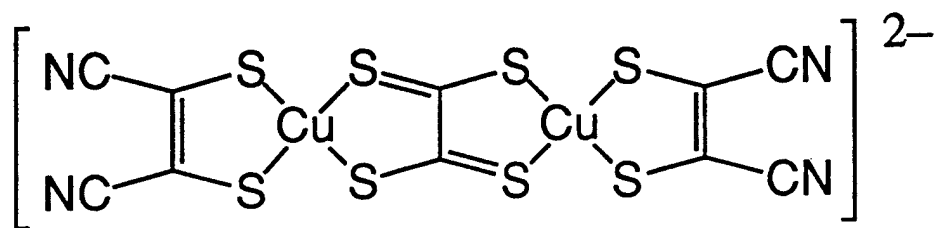


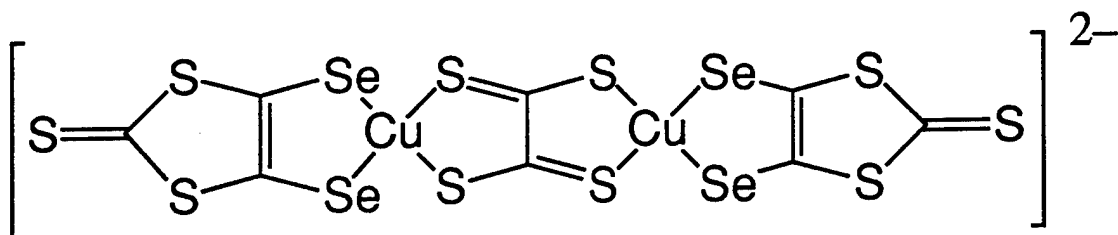
FIGURE 5



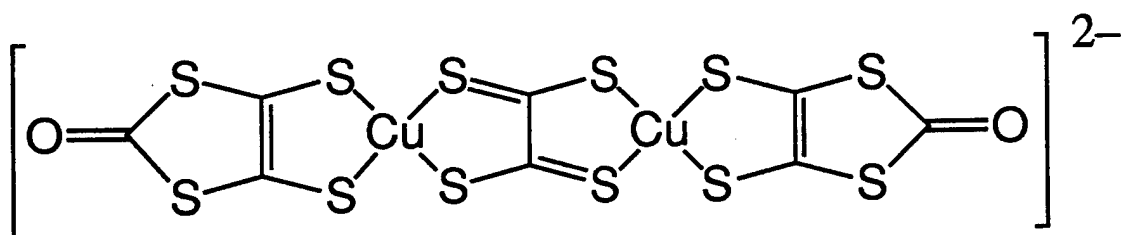
$(\text{Bu}_4\text{N})_2\{\text{tto}[\text{Cu}(\text{dmit})]_2\}$ (5)



$(\text{Bu}_4\text{N})_2\{\text{tto}[\text{Cu}(\text{mnt})]_2\}$ (6)



$(\text{Bu}_4\text{N})_2\{\text{tto}[\text{Cu}(\text{dsit})]_2\}$ (7)



$(\text{Bu}_4\text{N})_2\{\text{tto}[\text{Cu}(\text{dmid})]_2\}$ (8)

FIGURE 6

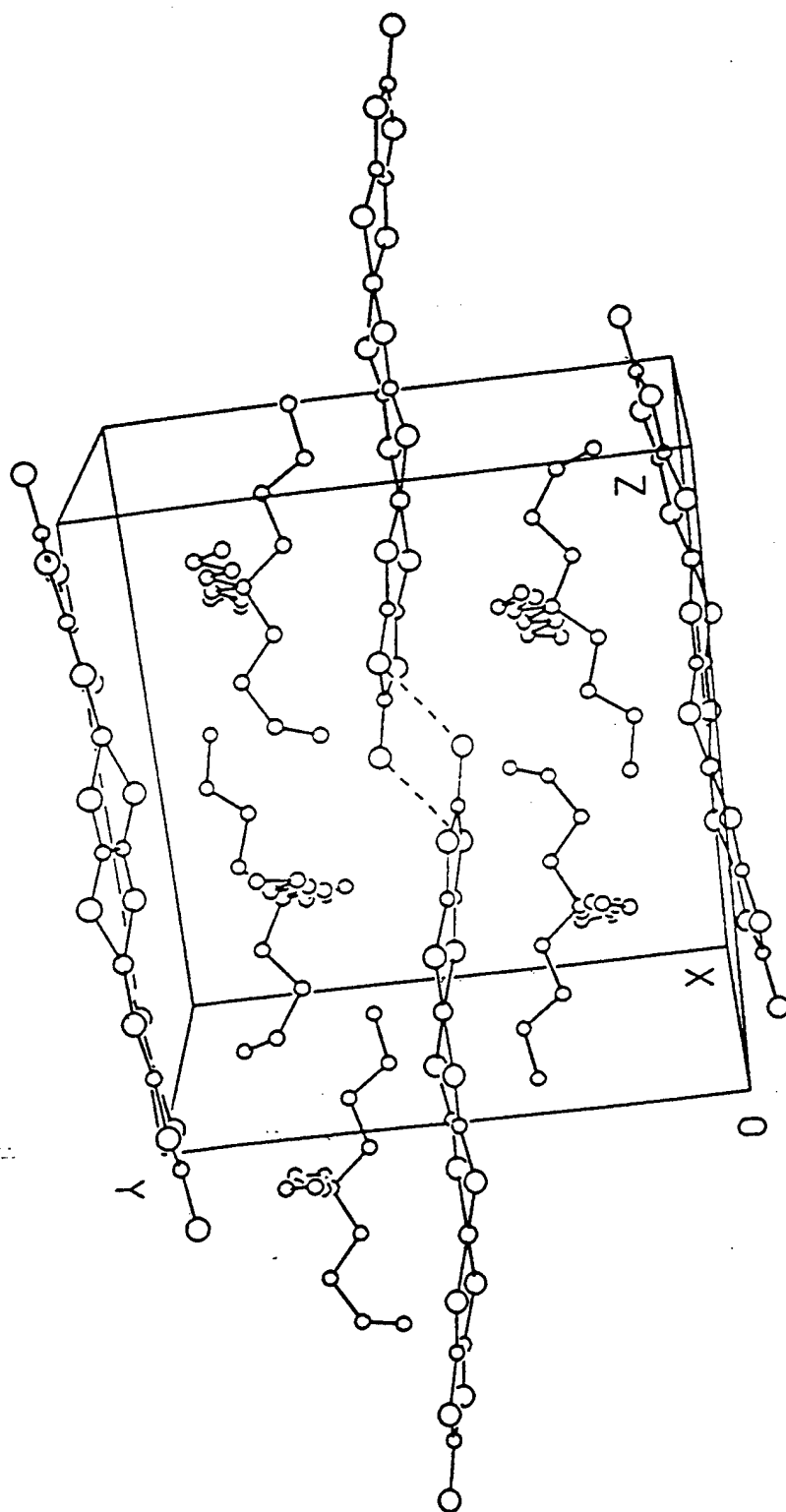


FIGURE 7

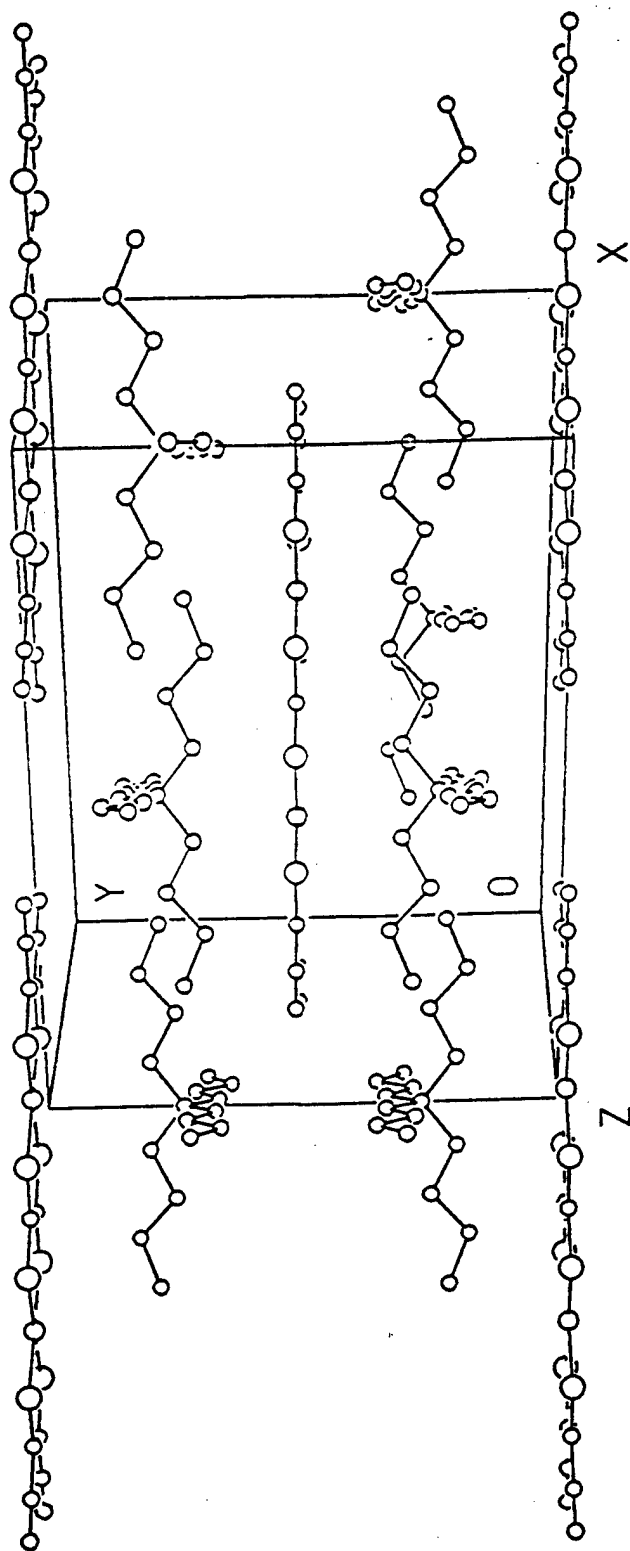


FIGURE 8

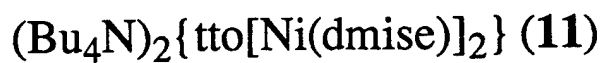
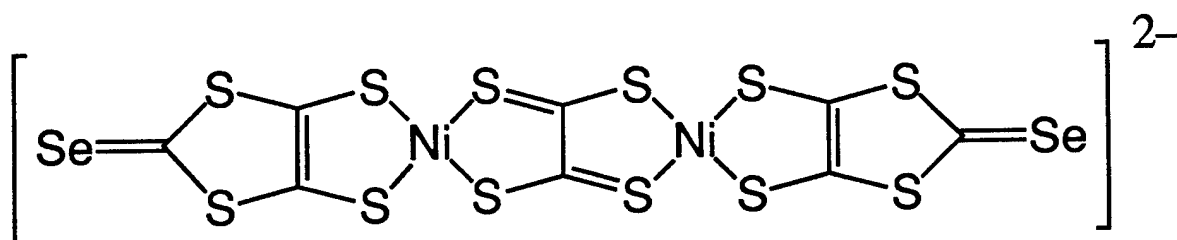
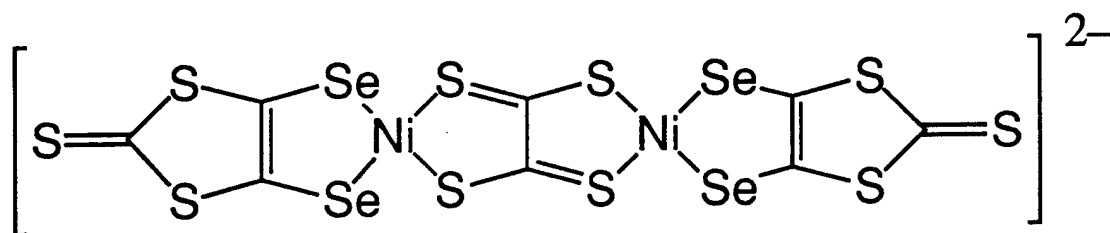
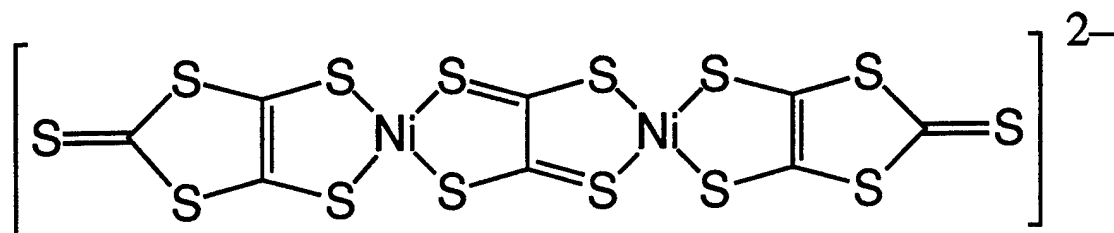


FIGURE 9

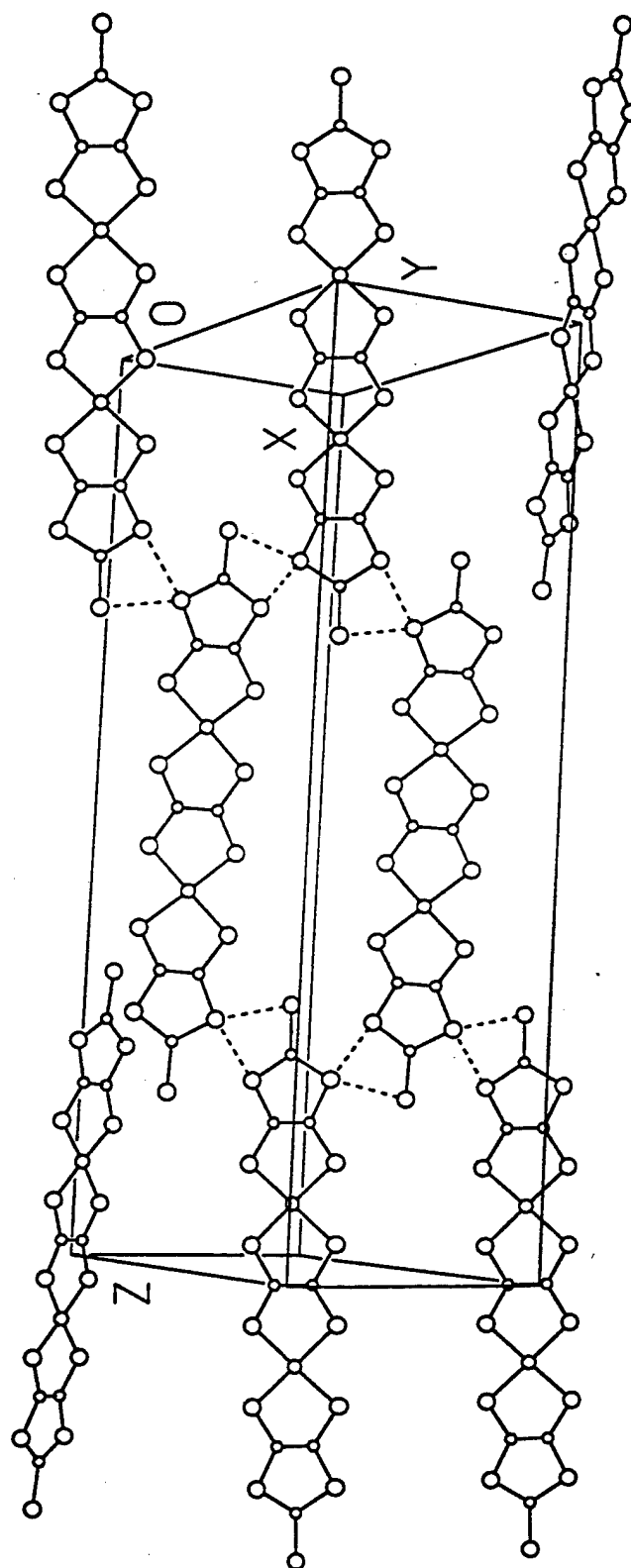
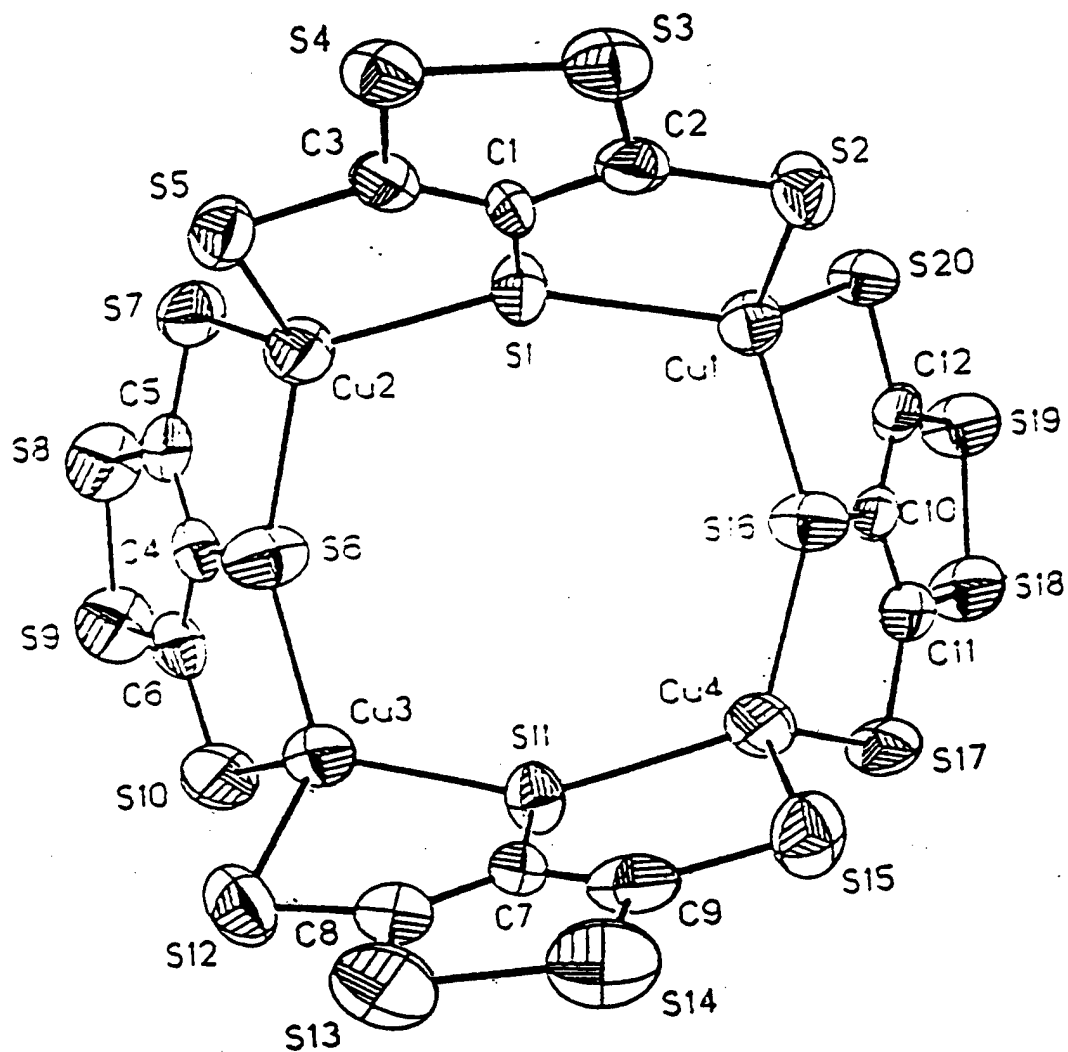


FIGURE 10



Personnel Supported

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Publications

1. Piotraschke, J.; Pullen, A. E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1995**, *34*, 4011.
2. Pullen, A. E.; Piotraschke, J.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1996**, *35*, 793.
3. Liu, H. -L.; Tanner, D. B.; Pullen, A. E.; Abboud, K. A.; Reynolds, J. R. *Phys. Rev. B*, **1996**, *53*, 10557.
4. Pullen, A. E.; Zeltner, S.; Olk, R. -M.; Hoyer, E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1996**, *35*, 4420.
5. Pullen, A. E.; Abboud, K. A.; Reynolds, J. R.; Piotraschke, J.; Zeltner, S.; Olk, R. M.; Hoyer, E.; Liu, H. L.; Tanner, D. B. "New Electrically Conducting Materials Based on the dmit Ligand", *Synth. Met.*, in press.
6. Pullen, A. E.; Olk, R. -M.; Zeltner, S.; Hoyer, E.; Abboud, K. A.; Reynolds, J. R. "A New Generation of [Ni(dmit)₂] Based Molecular Conductors", *Inorg. Chem.*, submitted for publication, 1996.
7. Pullen, A. E.; Liu, H. L.; Tanner, D. B.; Abboud, K. A.; Reynolds, J. R. "Electrocrystallization, Structure and Electronic Properties of the dmit-Based Salt (CH₃(C₆H₅)₃P)[Ni(dmit)₂]₃", *J. Mater. Chem.*, submitted for publication, 1996.
8. Pullen, A. E.; Zeltner, S.; Olk, R. M.; Hoyer, E.; Abboud, K. A.; Reynolds, J. R. "μ-Tetrathiooxalato Bridged Bimetallic Ni(II) Complexes. Synthesis, Crystal Structure Analysis, Electrochemical and Conductivity Behavior of Chalcogen-Rich, Extensively Conjugated and Planar Compounds" *Inorg. Chem.*, in preparation.

Interactions/Transitions

1. This work was presented at the Florida Advanced Materials Chemistry Conference Meeting, March 1995, in Palm Coast, FL.
2. This work was presented at the American Chemical Society National Meeting (Anaheim, CA, April 1995) in the Polymeric Materials Science and Engineering Division Symposium entitled "Polymeric and Organic Materials: Solid-State Properties and Smart Materials".
3. This work was presented at the American Physical Society Meeting, March 1995, in San Jose, CA.
4. This work was presented at the Florida Advanced Materials Chemistry Conference Meeting, March 1996, in Palm Coast, FL.
5. This work was presented at the American Chemical Society National Meeting (New Orleans, LA, April 1996) in the Inorganic Chemistry Division.
6. This work was presented at the International Conference on Science and Technology of Synthetic Metals (Snowbird, UT, August 1996) in the Symposium entitled "New Materials-Organics".

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